Degenerate ground states and nonunique potentials: breakdown and restoration of density functionals

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The Hohenberg-Kohn (HK) theorem is one of the most fundamental theorems of quantum mechanics, and constitutes the basis for the very successful density-functional approach to inhomogeneous interacting many-particle systems. Here we show that in formulations of density-functional theory (DFT) that employ more than one density variable, applied to systems with a degenerate ground state, there is a subtle loophole in the HK theorem, as all mappings between densities, wave functions and potentials can break down. Two weaker theorems which we prove here, the *joint-degeneracy theorem* and the *internal-energy theorem*, restore the internal, total and exchange-correlation energy functionals to the extent needed in applications of DFT to atomic, molecular and solid-state physics and quantum chemistry. The joint-degeneracy theorem constrains the nature of possible degeneracies in general many-body systems.

Introduction. Quantum mechanics is based on the assumption that all information that one can, in principle, extract from a system in a pure state at zero temperature is contained in its wave function. In nonrelativistic quantum mechanics the wave function obeys Schrödinger's equation,[1] which implies a powerful variational principle according to which the ground-state wave function minimizes the expectation value of the Hamiltonian. This variational principle was used by Hohenberg and Kohn (HK)[2] to show that the entire information contained in the wave function is also contained in the system's ground-state particle density $n(\mathbf{r})$.

HK established the existence of two mappings,

$$v(\mathbf{r}) \overset{1}{\Longleftrightarrow} \Psi(\mathbf{r}_1, \ldots \mathbf{r}_N) \overset{2}{\Longleftrightarrow} n(\mathbf{r}), \qquad (1)$$

where the first guarantees that the single-particle potential is a unique functional of the wave function, $v[\Psi]$, and the second implies that the ground-state wave function is a unique functional of the ground-state density, $\Psi[n]$. Taken together, both mappings are encapsulated in the single statement that the single-particle potential is a unique density functional $v[n]$. In this formulation, the HK theorem forms the basis of the spectacularly successful approach to many-body physics, electronic-structure theory and quantum chemistry that became known as density-functional theory (DFT).[3,4,5]

Mapping 2 was originally proven by contradiction[2] and later by constrained search.[6] Note that, in spite of occasional statements to the contrary in the literature, neither proof directly proves the combined mapping, and thus the existence of the functional $v[n]$. This requires additionally mapping 1, which in the case of density-only DFT is proven by inverting Schrödinger's equation[4,7]

$$\hat{V} = \sum_i v(\mathbf{r}_i) = E_k - \frac{(\hat{T} + \hat{U})\Psi_k(\mathbf{r}_1, \ldots \mathbf{r}_N)}{\Psi_k(\mathbf{r}_1, \ldots \mathbf{r}_N)}. \qquad (2)$$

According to the preceding equation, any eigenstate Ψ_k determines the single-particle potential $v(\mathbf{r})$ up to an additive constant, the corresponding eigenenergy.[8] The ground-state version of this equation is all one needs to prove mapping 1, and thus of the combined mapping $n(\mathbf{r}) \Rightarrow v(\mathbf{r}) + const$, which we write as $v = v[n]$. The constant can always be absorbed in the definition of the zero of energy, but the resulting nonuniqueness of the mapping $v[n]$ gives rise to derivative discontinuities[9] that crucially contribute to observables such as the band gap, chemical hardness, electron affinities, electron transfer energies, among others.

The two classic proofs of the HK theorem, by contradiction and by constrained search, have been extended to a wide variety of systems, including spin magnetization (in spin-density-functional theory – SDFT[10,11]) and orbital currents (in current-density-functional theory – CDFT[12]), among others. Further scrutiny, however, has led to the discovery of situations in which each of the two mappings breaks down.

Breakdown of mappings: Degeneracy. Mapping 2, $\Psi[n]$, breaks down in the presence of degenerate ground states, where neither the constrained search proof nor the proof by contradiction provide a unique wave function among the degenerate manifold, because the strict inequality of the underlying variational principle is replaced by the weaker relation less-or-equal. In the case of the proof by contradiction, the contradiction simply does not follow unless one has a strict inequality, and in the proof by constrained search there is no guarantee that the search delivers only one wave function for a specified density.

What remains from the proofs is that the ground-state density uniquely determines a manifold of degenerate states, $\{\Psi_i\}[n]$, but not all of these states individually.[13] Any member of this manifold, however, still uniquely determines the potential, since any of them can be used in Eq. (2). Hence, even in the presence of degeneracy, the mapping $v[\Psi_i]$, and thus $v[n]$, still exists. This situation is illustrated in black in Fig. 1.

To proceed from establishing mappings to a practi-

cal density-functional theory, one must define the total-energy functional $E_v[n]$, the universal internal-energy functional $F[n]$, and the exchange-correlation energy functional $E_{xc}[n]$. The Kohn-Sham formulation additionally requires the noninteracting kinetic-energy functional $T_s[n]$. 21 years after proving the original HK theorem, Kohn[14] showed how these functionals can be defined even if degeneracy renders the original proof ineffective.[4] Since all degenerate wave functions by definition yield the same ground-state energy E, one can directly define the functional

$$F[n] := E - \int d^3r\, n(\mathbf{r})v[n](\mathbf{r}) = E - V[n]. \quad (3)$$

Conventionally, this functional is defined as $F[n] = T[n] + U[n]$, but the information that the kinetic energy T and interaction energy U are density functionals is only available if the second mapping, $\Psi[n]$, holds, and cannot be taken for granted in the presence of degeneracy. By contrast, the alternative definition above only requires the mapping $v[n]$ to establish the existence of the universal internal-energy functional $F[n]$. Similarly, in the noninteracting KS system one defines

$$T_s[n] := E_s - \int d^3r\, n(\mathbf{r})v_s[n](\mathbf{r}) = E_s - V_s[n] \quad (4)$$

where $v_s(\mathbf{r})$ is the effective KS potential and E_s the ground-state energy of the KS system, i.e., the sum of the KS eigenvalues. The F and T_s functionals defined in this way can be used to establish a density variational principle for $E_v[n]$ and to define the exchange-correlation energy $E_{xc}[n] = F[n] - T_s[n] - E_H[n]$, where E_H is the Hartree energy.[4]

Thus tamed, degeneracy actually becomes helpful in further strengthening the foundations of DFT: on a lattice, any density can be written as a linear combination of densities arising from ensembles of degenerate ground states of a local potential, thus solving the discretized $v-$representability problem.[15]

Breakdown of mappings: Nonuniqueness. It is known[16] at least since 1983 that mapping 1, $v[\Psi]$, breaks down if finite basis sets are used to represent the wave functions. Harriman[16] gives both general arguments and an explicit example illustrating this breakdown. This breakdown of mapping 1 is the only one occuring already in the charge-density-only formulation of DFT, and it is manifestly an artifact of the use of a finite basis set.

In multi-density DFTs, such as SDFT and CDFT, the mapping between the set of effective potentials and the set of ground-state densities can break down even in the complete basis-set limit, because inversion of Schrödinger's equation does not establish a unique relation between the set of densities and the set of conjugate potentials. This is the so-called nonuniqueness problem of SDFT (and CDFT and others). Following an early observation of the problem by von Barth and Hedin,[10] the problem has been shown to be fundamental and pervasive in recent work by Eschrig and Pickett[17] and by two of us,[18] who provided explicit examples of different SDFT potentials sharing the same ground-state wave function. Ref. 18 proposed a classification of nonuniqueness into systematic (arising from the existence of certain constants of motion) and accidental (arising from special features of the ground state). In both cases, the nonuniqueness is associated with the external potential. Since the mapping $\Psi[n]$ remains intact, and internal-energy functionals can be defined exclusively in terms of wave functions,

$$F[n] = \langle \Psi[n]|\hat{T} + \hat{U}|\Psi[n]\rangle, \quad (5)$$

the functionals $E_v[n] = F[n] + V[n]$, $T_s[n] = \langle \Phi[n]|\hat{T}|\Phi[n]\rangle$, and $E_{xc}[n] = F[n] - E_H[n] - T_s[n]$ still exist.

Additional examples of both systematic and accidental nonuniqueness were found in CDFT[19] and in SDFT on a lattice.[20] The extent to which nonuniqueness of the potentials affects various types of applications of multi-density DFTs, as well as possible remedies, are discussed in Refs. 19,20,21.

Breakdown of mappings: Nonuniqueness and *degeneracy.* We have just seen that in the presence of nonuniqueness the mapping $v[\Psi]$ breaks down, whereas in the presence of degeneracy the mapping $\Psi[n]$ breaks down. Interestingly, a crucial fact has been overlooked in the standard analysis of either degeneracy or nonuniqueness: These complications can occur simultaneously! If a system with a degenerate ground state is treated with SDFT or any other formulation of DFT suffering from a nonuniqueness problem, none of the mappings holds, and no conventional HK theorem exists. In fact, it is $\Psi[n]$ that was used above to define $F[n]$, $T_s[n]$ and $E_{xc}[n]$ in the absence of $v[\Psi]$ (nonuniqueness), while $v[\Psi]$ guaranteed the existence of $v[n]$ and thus of $F[n]$, $T_s[n]$ and $E_{xc}[n]$ in the absence of $\Psi[n]$ (degeneracy). If both $\Psi[n]$ and $v[\Psi]$ break down, it seems nothing is left. The breakdown of both mappings is illustrated in Fig. 1. Three simple examples are given below.

Our first example is an extension of the case of the noninteracting Li atom[13] to collinear SDFT. If the spin degree of freedom is included, each of the four degenerate states[13] is additionally twofold degenerate with respect to S_z. The set of external potentials $B = 0, v = 3/r$ thus has an 8-fold degenerate ground-state manifold. The Slater determinants formed from the configurations $1s^2 2p^+ \uparrow$ and $1s^2 2p^- \uparrow$ have the same charge and spin densities. Again, we see that in the presence of a degenerate ground state the densities do not uniquely determine the wave function. Differently from above, in SDFT we can now also consider the alternative set of external potentials $B' = const \neq 0, v = 3/r$. The spin-only magnetic field B simply splits the ground-state manifold into two, one comprising the four spin-up configurations, the other the four spin-down configurations. The new ground state will be in the spin-up manifold, where the configurations $1s^2 2p^+ \uparrow$ and $1s^2 2p^- \uparrow$ remain and still yield the same densities. From the point of view of the mapping

between densities and potentials, this is simply the by now well known[17,18,19,20,21] nonuniqueness of the potentials of SDFT with respect to a weak collinear magnetic field. The full situation, however, is now one in which the densities do not determine the wave functions but only a (ground-state) manifold of them, and some members of these manifolds are ground states in more than one set of external potentials. The functionals $\Psi[n]$, $V[\Psi]$ and $V[n]$ thus do not exist.

Consider next an interacting atom in an $S = 1$, $L = 1$ state. Concrete examples are ^{6}C and ^{14}Si (with term $^3P_0$) and ^{8}O and ^{16}S (with term $^3P_2$). In the set of external potentials $B = 0, v = Z/r$ the ground state of such systems is $(2L+1)(2S+1) = 9$-fold degenerate. Let's denote the members of this manifold as Ψ_{L_z, S_z}. Several of these, such as $\Psi_{1,1}$ and $\Psi_{-1,1}$ have the same charge and spin densities. Hence, we have another situation in which these densities do not determine the wave functions but only the manifold. Now consider the same system in external potentials $B' = const \neq 0$ and $v = Z/r$. The states $\Psi_{1,1}$, $\Psi_{0,1}$ and $\Psi_{-1,1}$ remain degenerate ground states in this new set of potentials, and the density and spin density of the first and the last are still the same as for $B' = 0$. Hence, as in other examples of nonuniqueness, knowledge of this state alone does not determine the external potentials. Upon combining both observations we find that to a given set of ground-state densities (n, m) there may correspond more than one degenerate wave function (all in external potentials $B = 0, v = Z/r$), and all of these wave functions are also degenerate ground-states of the different set of external potentials (B', v). Again, the functionals $\Psi[n]$, $V[\Psi]$ and $V[n]$ do not exist.

Lastly, we discuss a modification of the one-electron example by von Barth and Hedin.[10] Consider a single electron in the presence of an external 4-potential $w_{\alpha\beta}(\mathbf{r}) = V(\mathbf{r})\delta_{\alpha\beta} - [\mathbf{B}(\mathbf{r}) \cdot \vec{\sigma}]_{\alpha\beta}$, where $\vec{\sigma}$ is the vector of Pauli matrices. Let $w_{\alpha\beta}(\mathbf{r})$ be uniform along one spatial direction (say, x), with periodic boundary conditions along that direction separated by a distance L (which is topologically equivalent to confining the electron on a ring). The two-fold degenerate ground state of the Hamiltonian $H_{\alpha\beta} = -\frac{\hbar^2}{2m}\delta_{\alpha\beta} + w_{\alpha\beta}(\mathbf{r})$ is given by $\Psi_\alpha^\pm(\mathbf{r}) = e^{\pm ikx}\psi_\alpha(y,z)$, $k = 2\pi/L$, with both ground states producing the same density. Furthermore, both ground states $\Psi_\alpha^\pm(\mathbf{r})$ are invariant under perturbations $w'_{\alpha\beta}(\mathbf{r}) = V'(\mathbf{r})\{\delta_{\alpha\beta} - [\mathbf{m}(\mathbf{r}) \cdot \vec{\sigma}/n(\mathbf{r})]_{\alpha\beta}\}$, where $n(\mathbf{r})$ and $\mathbf{m}(\mathbf{r})$ are the ground-state density and magnetization, and $V'(\mathbf{r})$ is an arbitrary (but not too large) scalar potential function. Thus, we have found another case where both mappings (1) break down.

Restoration of energy functionals. The question then arises whether the energy functionals $E_v[n]$, $F[n]$, $T_s[n]$ and $E_{xc}[n]$ can still be defined, even in the absence of all mappings that are conventionally considered the content of the HK theorem. To answer affirmatively, we consider two distinct cases, represented in Fig. 2. In case I, Ψ_a and Ψ_b, which both produce density n, are degenerate ground states in potentials V_1 and V_2. In case II only

Ψ_b is common ground state of both potentials, whereas Ψ_a is ground state only of V_1, but either an excited state or not even an eigenstate at all in V_2. We first prove that case II cannot occur. In potential V_1, we define the internal energy (not yet a functional of any density) as

$$F_1 = E_1 - \int d^3 r v_1(\mathbf{r})n(\mathbf{r}). \tag{6}$$

In potential V_1, Ψ_a and Ψ_b are degenerate, so that $E_1 = \langle\Psi_a|\hat{T} + \hat{U} + \hat{V}_1|\Psi_a\rangle = \langle\Psi_b|\hat{T} + \hat{U} + \hat{V}_1|\Psi_b\rangle$. Since both also produce the same density, the expectation value of $\hat{V}_1$ with Ψ_a and Ψ_b is the same, so that

$$\langle\Psi_a|\hat{T} + \hat{U}|\Psi_a\rangle = \langle\Psi_b|\hat{T} + \hat{U}|\Psi_b\rangle = F_1 \tag{7}$$

is independent of the choice of wave function. Next, applying the variational principle to the Hamiltonian of system 2, we have

$$\langle\Psi_a|\hat{T} + \hat{U} + \hat{V}_2|\Psi_a\rangle > E_2, \tag{8}$$

with a strict inequality, as by assumption Ψ_a in potential 2 is not degenerate with the ground state of that system. From Eq. (7), and again making use of the fact that Ψ_a and Ψ_b produce the same density, we can write this as

$$\langle\Psi_b|\hat{T} + \hat{U} + \hat{V}_2|\Psi_b\rangle = E_2 > E_2. \tag{9}$$

The contradiction proves that case II cannot occur. This result is completely general, and implies the following theorem: *Consider two degenerate ground-state wave functions in potential V_1, Ψ_a and Ψ_b. The constraint that these two wave functions have the same density guarantees that in any other potential V_2 either both are ground states (and thus also degenerate) or none of them is.* We call this the *joint-degeneracy* theorem. Note that all of our explicit examples above respect the joint-degeneracy theorem.

Even though one could formally define an $F[n]$ functional in case II, we have just shown that that case cannot occur, so we only need to establish the existence of $F[n]$ in case I. In analogy to Eq. (6), we define in potential V_2

$$F_2 = E_2 - \int d^3 r v_2(\mathbf{r})n(\mathbf{r}). \tag{10}$$

Since Ψ_a and Ψ_b are degenerate also in potential V_2, we have $E_2 = \langle\Psi_a|\hat{T} + \hat{U} + \hat{V}_2|\Psi_a\rangle = \langle\Psi_b|\hat{T} + \hat{U} + \hat{V}_2|\Psi_b\rangle$, resulting in

$$F_2 = \langle\Psi_a|\hat{T} + \hat{U}|\Psi_a\rangle = \langle\Psi_b|\hat{T} + \hat{U}|\Psi_b\rangle, \tag{11}$$

where we again used that Ψ_a and Ψ_b yield the same density. This is the same equation obtained above for F_1. Again, this result is completely general, implying the following theorem: *Regardless of any possible degeneracy or nonuniqueness, two systems with same ground-state density have the same internal energy F. Hence, the functional $F[n]$ exists and is universal, i.e., independent of the potentials.* This *internal-energy theorem* is consistent

with the constrained-search formulation of DFT,[6] which defines $F[n] := \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle$, although in the presence of degeneracy this definition cannot be used to define $\Psi[n]$.

Since the noninteracting kinetic energy T_s is the internal energy of the Kohn-Sham system, it is also a well-defined density functional, and $E_{xc}[n] = F[n] - E_H[n] - T_s[n]$ can be constructed as usual. Finally, for a given external potential, the functional $E_v[n]$ then obviously also exists.

Conclusions. We have shown both by general arguments and by specific examples that in the case of degeneracy in multi-density DFTs all three mappings, $\Psi[n]$, $V[\psi]$ and $V[n]$, and thus the entire body of information usually considered the content of the HK theorem,

break down. The weaker *joint-degeneracy* and *internal-energy theorems*, however, still allow the definition of the internal-energy functional $F[n]$, and thus also the functionals $T_s[n]$, $E_v[n]$ and $E_{xc}[n]$. Practical DFT, which assumes the existence of these functionals, is thus largely unaffected by the breakdown of the various mappings. However, we stress that we have only proven existence of the functionals, not their differentiability. In fact, in the presence of nonuniqueness, all these functionals are expected to display derivative discontinuities.

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[13] A textbook example[4,22] is the noninteracting Li atom with the four degenerate ground state configurations $1s^2 2s$, $1s^2 2p^+$, $1s^2 2p^0$ and $1s^2 2p^-$. Slater determinants formed from the second and fourth configuration are distinct wave functions that have the same density $n(\mathbf{r})$ and arise from the same external potential.

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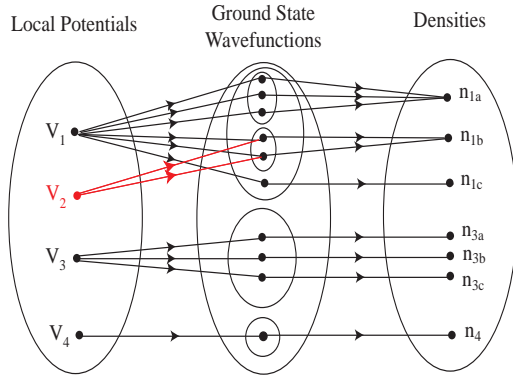
FIG. 1: (color online) Schematic illustration of the breakdown of mappings that occurs in the presence of degeneracy (black) and the additional complication posed by nonuniqueness (red). V and n stand generically for sets of conjugate potentials and densities (e.g., $v_\uparrow, v_\downarrow$ and $n_\uparrow, n_\downarrow$ in SDFT). Large ovals are sets of functions, medium-size ovals collect degenerate wave functions, and small ovals enclose degenerate wave functions that give rise to the same density.
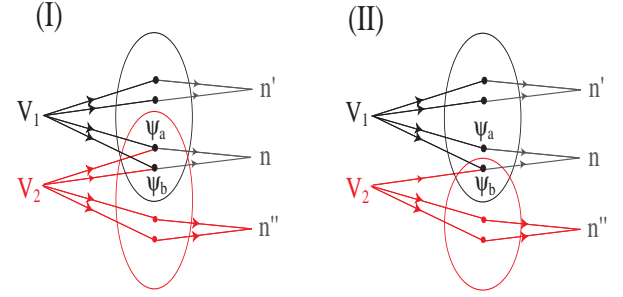

FIG. 2: (color online) The joint-degeneracy theorem (case I) and a situation excluded by it (case II). Colored ovals enclose degenerate wave functions coming from a local potential.